

# Photocatalytic Oxidation of Organophosphorus Pesticides using Zinc Oxide

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## Abstract

*In recent years, the application of heteroge-neous photocatalytic water treatment processes has gained wide attention due to its effectiveness in degra-ding and mineralizing the pesticides. These pesticides are often found in many surface and groundwater sources and their concentration levels often exceed the drinking water permissible limits recommended by Iran and European drinking water standards. The aim of the present study was to investigate the influence of various parameters such as initial malathion and diazinon concentration catalyst amount, initial pH of the reaction medium and pesticide types on the photo-catalytic decomposition of pesticides in the presence of ZnO using an ultraviolet lamp as the light source. The best conditions for the photocatalytic degradation of pesticides were obtained. Results showed that the optimal concentration of catalyst was found to be 100 mg. L<sup>-1</sup>. The photodegradation efficiency of pesticides increases with the increase of the illumination time. The photodegradation rate of pesticides was higher in alkaline than in acidic conditions. The photocatalytic degradation rate of the malathion was more than diazinon. The photodegradation efficiency decreases with the increase in the initial concentration of pesticides. The photocatalytic system afforded the highest removed percentage at initial concentration for diazinon and malathion were 100 and 200 mg.L<sup>-1</sup> respectively.*

**Keywords:** Malathion, diazinon, zinc oxide, photodegradation.

## Introduction

Organophosphorous pesticides like malathion and diazinon are commonly used in Iran for increasing agricultural productivity and they are detected in various environmental matrices such as soil and water because of their widespread use<sup>1</sup>. Surface water and ground water pollution not only affect the health of human being as it is being used for drinking, but also can act as sources of contamination for food chain, when used for irrigation<sup>2</sup>. Regrettably, a great number of pesticides are non-biodegradable. Therefore biological process and conventional process are not the ideal process and other more effective technologies such as advanced oxidation technologies (AOTS) have been proposed for treatment of polluted water by pesticides<sup>3-4</sup>.

Different treatment technologies are available for the removal of pesticide contamination from surface and groundwater sources. Among these advanced oxidation process (AOP) such as photo oxidation seems to be very effective specifically at low concentration of pesticides<sup>5-6</sup>. Though photocatalytic degradation of pesticide using ZnO under UV light is possible, it may not be a practical proposition for the treatment of drinking water due to high operation cost. Utilization of visible and solar radiation for the photo-catalytic oxidation is one of the simple and economic alternatives for the drinking water treatment.

These technologies allow pesticides to be removed by mineralization. Photolysis is one of the major transformation processes affecting the fate of pesticides in aquatic environment. Photocatalytic oxidation by semiconductor oxides is an area of environment interest for treatment of polluted water<sup>7-8</sup>. Several catalysts have been used, and among them TiO<sub>2</sub> is one of the most effective<sup>9-10</sup>. ZnO is frequently used. The most advantage of ZnO in comparison to TiO<sub>2</sub> is that it absorbs over a large fraction of the UV range and the equivalent threshold wavelength of ZnO is 387nm<sup>11</sup>. ZnO is also a very interesting wide band gap semiconductor material, because of its direct band gap, large excitation binding energy and piezo electric properties<sup>12</sup>. Few reports have used UV/ZnO for degradation of organic pollutants<sup>13-16</sup>.

## Material and methods

The ZnO catalyst was sourced from FLUKA. The diameter specific surface area and band gap energy of ZnO were 14 nm, 10 m<sup>2</sup>.g<sup>-1</sup> and 2.92 eV respectively. The tested compounds in this study diazinon and malathion (from supelco), NaOH, HNO<sub>3</sub> were obtained from Merck Co. (Germany). The concentration of malathion in samples was 200, 400, 600 µg.L<sup>-1</sup>. The concentration of diazinon in samples was 100, 300, 500 µg.L<sup>-1</sup> and used 30% insecticides. The pH of the samples solution malathion and diazinon was 3, 7, 9 and reaction temperature is 25 ± 1°C. For the photodegradation of diazinon and malathion a solution containing known concentration of the pesticides and ZnO nanopowder was prepared and it was allowed to equilibrate for 30 min in the darkness, then 50 ml of the prepared suspension was transferred to a 800 ml Pyrex reactor.

Irradiation was carried out with a 125 w medium pressure mercury lamp (Philips, Holland), which was above the batch photo reactor. The distance between solution and UV source was constant, 3.75 cm in all experiments. In the

surface of solution the light intensity was  $80 \text{ W m}^{-2}$  that was measured by Hagner – Detector (EC1- UV-C, Swede). pH values were measured with pH meter (Sartorius, Germany). After that, the lamp was switched on to initiate the reaction. During irradiation, agitation was maintained by magnetic stirrer (IKA, Werke, Germany) to keep the suspension homogeneous and the suspension was sampled after an appropriate illumination time. Temperature  $25 \pm 1^\circ\text{C}$  was maintained by circulating water in a double jacket cooling array. For the extraction of diazinon and malathion, techniques (DLLME) dispersive liquid – liquid microextraction<sup>17</sup> were used

A 5 ml of sample (water + analyte) was mixed with 500 ml extraction solution (2 ml internal standard: chlorpyrifos  $1000 \text{ mg L}^{-1}$ , 10 ml chloroform with 100 ml acetone). The mixture was then centrifuged for 5 min at 3500 rpm. After this process, the upper aqueous phase was collected by pipette; the droplets were sedimented at the bottom of the conical test tube. For identification, 1ml samples were injected into the GC-MS (Varian CP-3800 GC with MS trap detector Varian Saturn 2200, run in EI mode). Injector temperature was  $270^\circ\text{C}$  and analysis was done using a capillary column (Varian DB-5 column; 30m  $250 \mu\text{m}$  I.D., film thickness  $0.25 \mu\text{m}$ ). The method started at  $150^\circ\text{C}$ , which was held for 2 min, then ramped to  $120^\circ\text{C}$  at a rate of  $25^\circ\text{C}/\text{min}$ , followed by an increase to  $270^\circ\text{C}$  (held for 2 min). The method used a split split ratio 1:10. Helium (99.999%) was used as carrier gas at 1 ml/min. Data were analyzed using T – test, ANOVA one way test using SPSS software.

## Results and Discussion

**Effect of catalyst amount:** Effect of catalyst amount is the concentration of malathion at irradiation time shown in fig. 1, 2. Effect of catalyst amount is the concentration of diazinon at irradiation time is shown in fig. 3 and 4. As the concentration of ZnO is increased, the removed percentage also increased. The highest remove percentage was observed when  $100 \text{ mg L}^{-1}$  of ZnO was used. The results indicated that the degree of photodegradation increases with catalyst loading and then decreases at high values because of high scattering and screening effects. The tendency to words agglomeration (particle – particle interaction) also increases at high solids concentration. Although the number of active sites in solution will increase with catalyst loading, a point appears to be reaches where light penetration is compromised because of excessive particle concentration. Further increase in catalyst loading beyond the optimum will result in non-uniform light intensity distribution so that the reaction rate would indeed be lower with increased catalyst dosage. Generally, the amount of photocatalyst to be used should maintain a balance between these two opposing effects in order to ensure efficient absorption of photons and to avoid excess catalyst, the photocatalytic reactor should be operated at optimum catalyst loading. Consistently similar results have been reported for degradation of metamitron,

terephthalic acid and 2-4- dinitrophenol<sup>18-20</sup>.

**Effect of pH values:** An important parameter in the photocatalysed degradation of pesticides is pH of the solution because it influences the surface charge of the semiconductor. In our case, the experiments were carried out at an initial pH of 3, 7 and 9. The removed percentage of UV/ZnO system was determined at pH 3, 7 and 9 (Fig 5). The K values for the UV/ZnO system increased with pH (Table 1, 2). The results indicated that the degree of photodegradation increased with increasing pH. Generally characteristics of organic pollutants in aqueous solution differ greatly is several parameters, particularly in their speciation behavior, solubility in water and hydrophobicity. At pH below its pKa value, an organic compound exists as neutral state. Above this pKa value, organic compound attains a negative charge.

Some compounds can exist in positive, neutral and negative forms in aqueous solutions. This variation can also significantly influence their photo-catalytic degradation behavior<sup>21</sup>. The pH at which the surface of an oxide is uncharged is defined as the zero point charge (pHzpc). The surface of the catalyst is positive below pH 9.0<sup>22</sup>. For example pKa for diazinon is 2.60. The effect of pH on the photocatalytic performance can be thus explained in terms of electrostatic interaction between the catalyst surface and the target substrate. Diazinon is negatively charged above pH 2.6, as catalysts are positively charged below pH= 9. Optimal conditions were found at which the positively charged ZnO and negatively charged insecticide molecules should readily attract each other.

According to some authors,<sup>18,23</sup> the maximum effectiveness for the ZnO system occurs between pH 6 and 8. At acidic pH, ZnO can react with acids to produce the corresponding salt and at alkalic pH, it can react with a base to form some complexes. The result is the dissolution and photodissolution of ZnO in those cases and in consequence a decrease in the reaction rates. Therefore the pH of the solution can play ally role in the adsorption and photocatalytic oxidation of pollutants. Similar observations have also been made for the degradation of methamidophos, carbofuran and thiram<sup>24-26</sup>.

## Effect of initial concentration and pesticide type:

The influence of initial concentration of pesticides (malathion and diazinon) on the photocatalytic degradation is an important aspect of the study. The results are illustrated in fig 6. The degree of photodegradation decreased with increasing of initial concentration of pesticide. The photodegradation efficiency of malathion decreases from 73.58% to 65.3% when the initial concentration increases from 200 to  $600 \mu\text{g/L}$  and for diazinon decreases from 69.88 % to 55.2% when the initial concentration increases from 100 to  $500 \mu\text{g/L}$ . An increase in substrate concentration can lead to the generation of intermediates which may adsorb on the surface of the catalyst. Slow diffusion of the generated

intermediates from the catalyst surface can result in the deactivation of active sites on the photocatalyst and result in a reduction in the degradation rate. Also when the initial pesticide concentration increases, the amount of dye adsorbed on the catalytic surface also increases. This reduces the light absorption of the catalyst consequently lowering the catalytic activity.

The increase in pesticide concentration decreases solution transparency and consequently the path length of photon entering into the pesticide solution also decreases. At higher pesticide concentration a significant amount of UV light may be absorbed by the pesticide molecule rather than the catalyst and this may also reduce the catalytic efficiency.<sup>27-28</sup> Also, a lower photodegradation rate was observed with increasing initial concentration of malathion and diazinon in UV/ZnO system. The rate of photodegradation is related to the formation of OH radicals which are formed through the reaction of valance band holes with adsorbed H<sub>2</sub>O and OH<sup>-</sup>. At high concentration of pesticides, adsorbed OH<sup>-</sup> ions would have been replaced by pesticides which would have reduced the production of OH radicals. This maybe the reason for the reduction in reaction rate with increase in concentration of pesticides<sup>25,29</sup>. The effect of type pesticide on the photocatalytic degradation obtained result are illustrated in table 1, 2. The results indicated that the photocatalytic degradation rate of the malathion was more than diazinon.

The effect of the synergetic on the photocatalytic was studied and the obtained results are presented in table 1, 2 and fig 7. From table 1, 2, it can be seen at pH 7, the degradation rate constants of UV/ZnO and UV were 0.0281, 0.0191 and 0.0262, 0.0172 (S<sup>-1</sup>) for malathion and diazinon respectively, also from fig 7 the removal mean percent of the process UV/ZnO was more than that of UV process. The ability of the semiconductor to act as sensitizer and consequently to enhance the photocatalysed degradation of the pesticides studied can be attributed to its electronic structure which is characterized by filled valence band and an empty conduction band. When ZnO is illuminated with energy higher than its band gap energy, electron/hole pairs are produced: ZnO + hv (<380 nm) → h<sup>+</sup> + e<sup>-</sup>.

These species can either recombine or react with electron donors or electron acceptors which are adsorbed on the semiconductor surface or trapped within the surrounding electrical double layer of the charged particles and to produce hydroxyl radicals (·OH) which can promote the oxidation of pesticides<sup>30</sup>. Various researches reported that the process of photocatalysis was more effective than that of photolysis for the removal of organic pollutants from aqueous solutions for example: the removal efficiency of metamitron by UV/ZnO was higher than UV, the degradation of eight pesticides by the synergetic process of photocatalysis and photocatalytic oxidation of phenolic compounds was higher than photolysis<sup>18, 22, 31</sup>.

**Effect of irradiation time:** The effect of the time on the photocatalytic was studied and the obtained results are presented in fig 8. The degree of photodegradation increased with increasing of irradiation time. The removal mean of malathion increases from 51.27% to 95.68% when the time irradiation increases from 60 to 180 S and for diazinon increases from 37.92 % to 86. 74% when the time irradiation increases from 60 to 180 S.

The photocatalytic degradation of the pesticides take place on the surface of ZnO where ·OH and O<sub>2</sub><sup>-</sup> radicals are trapped in the holes of reactive species. Oxygen and water are essential for photocatalytic degradation. The ·OH radicals are strong enough to break the bonds in the pesticide molecules adsorbed on the surface of ZnO. The amount of ZnO and concentration of pesticides are constant, the number of ·OH and O<sub>2</sub><sup>-</sup> radicals increases with the increase in the irradiation period and hence the pesticide molecules are completely degraded into smaller fragments<sup>13, 32</sup>.

## Conclusion

This study demonstrates the heterogeneous photocatalytic system and its usefulness for water treatment. The role of various operating parameters on the photocatalytic degradation of various pesticides such as initial concentration catalyst amount, initial pH of the reaction medium, time, and pesticide types can significantly influence the photocatalytic degradation rate of pesticides. The obtained results indicate that the photodegradation of pesticides were affected by the concentration of ZnO, the initial pesticide concentration and initial pH. Alkaline media were favorable for the photocatalytic degradation of pesticides. The photodegradation efficiency decreased with an increase in the initial concentration of pesticides. The use of solar photocatalysis in the presence of ZnO as photosensitizers constitutes a very effective and rapid method for the reduction and even elimination of these pesticides in water.

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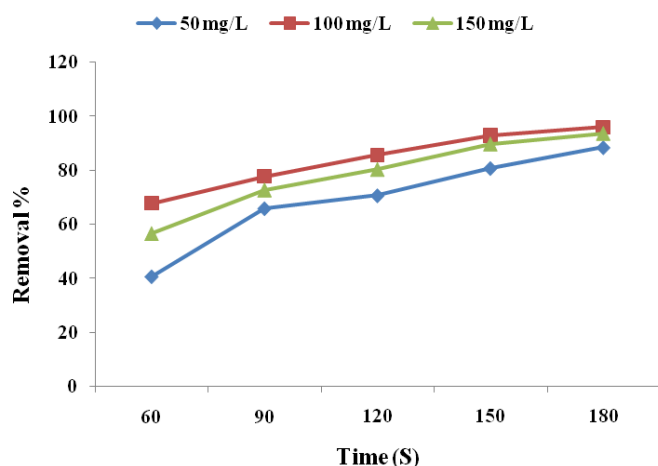


Fig.1: Comparisons of removal percentage in UV/ZnO system of malathion at different catalyst dose malathion = 200  $\mu\text{g.L}^{-1}$  and pH=7

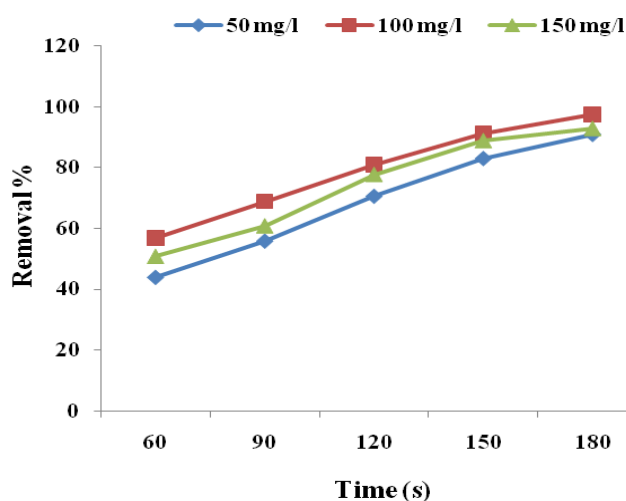


Fig.2: Comparisons of removal percentage in UV/ZnO system of malathion at different catalyst dose malathion = 600  $\mu\text{g.L}^{-1}$  and pH=9

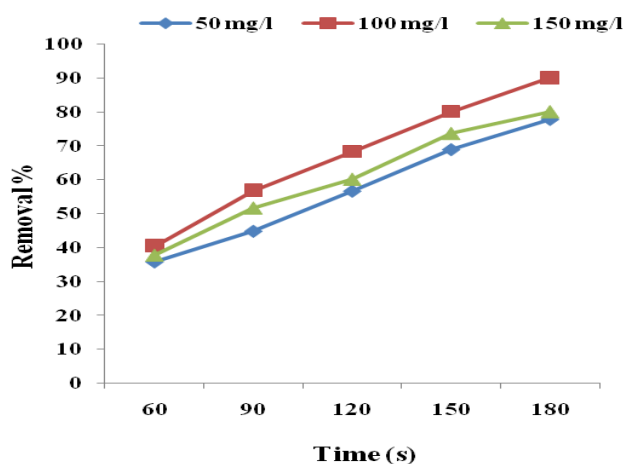


Fig.3: Comparisons of removal percentage in UV/ZnO system of diazinon at different catalyst dose diazinon = 100  $\mu\text{g.L}^{-1}$  and pH=7

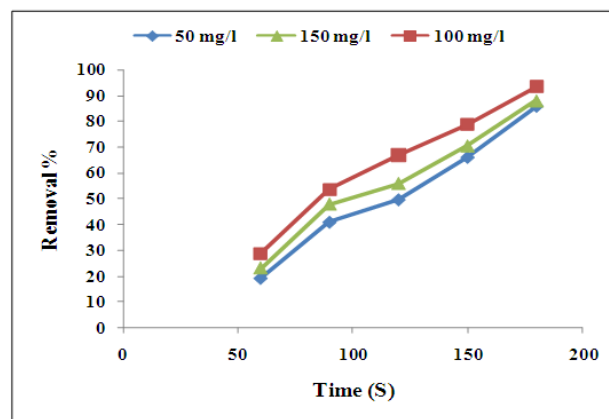


Fig.4: Comparisons of removal percentage in UV/ZnO system of diazinon at different catalyst dose diazinon = 500  $\mu\text{g.L}^{-1}$  and pH=9

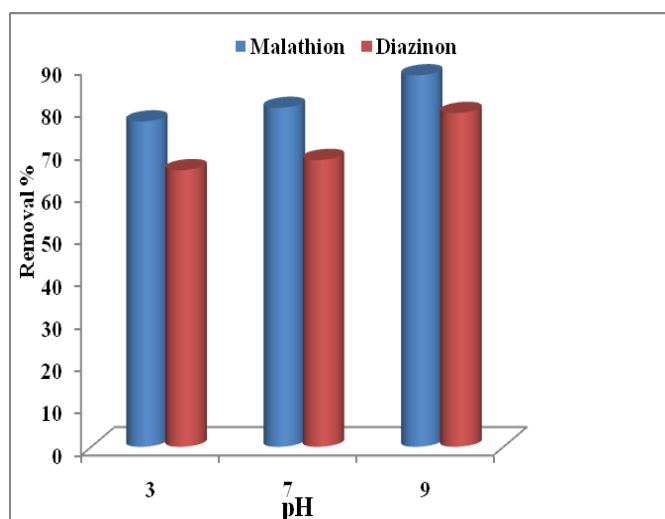


Fig.5: comparison of removal percentage in UV/ZnO system of pesticides at different pH

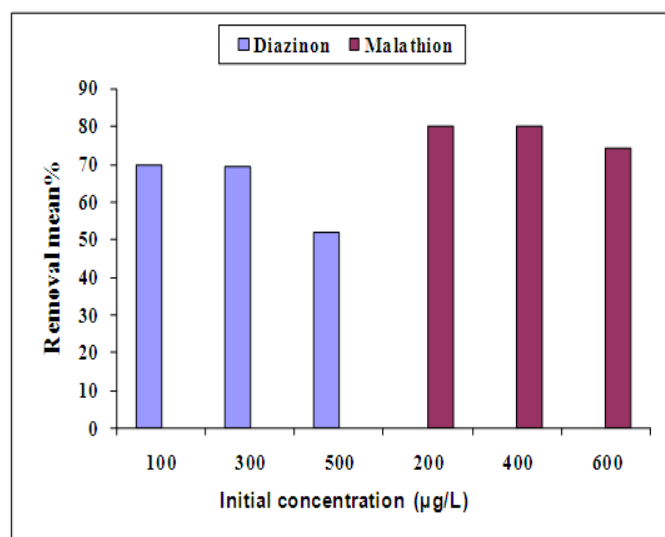
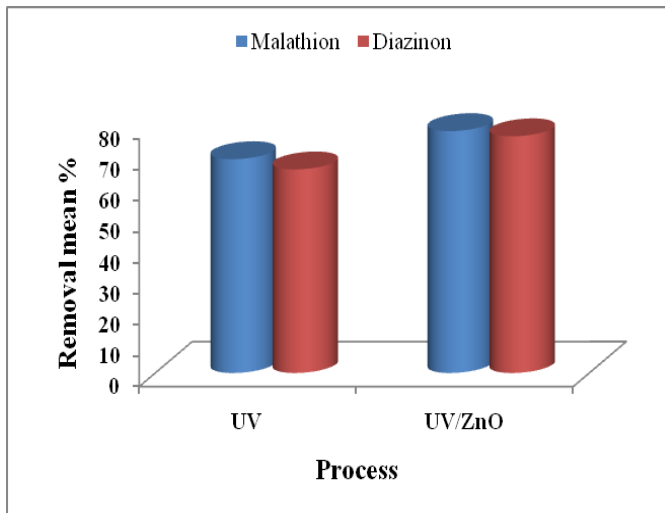
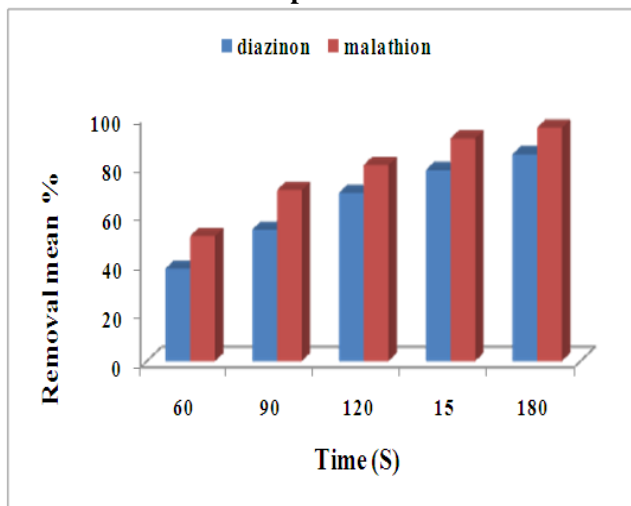


Fig.6: Comparison of removal percentage in UV/ZnO system of pesticides at different concentration



**Fig.7: Comparison removal of mean pesticides at different processes**



**Fig. 8: Comparison removal of mean pesticides at different time**

**Table1**

**The reaction rate constants for photodegradation of diazinon ( $\text{Co}=100 \mu\text{g.L}^{-1}$ ) and  $\text{ZnO}=100 \text{mg.L}^{-1}$  at different pH**

Systems	$\text{K}(\text{S}^{-1})$	$\text{r}^2$
UV(pH 3)	0.0151	0.9421
UV(pH 7)	0.0172	0.9581
UV(pH 9)	0.0193	0.9428
UV/ZnO(pH 3)	0.0241	0.9569
UV/ZnO (pH 7)	0.0262	0.9917
UV/ZnO (pH 9)	0.0310	0.8954

**Table2**

**The reaction rate constants for photodegradation of malathion ( $\text{Co}=200 \mu\text{g.L}^{-1}$ ) and  $\text{ZnO}=100 \text{mg.L}^{-1}$  at different pH**

Systems	$\text{K}(\text{S}^{-1})$	$\text{r}^2$
UV(pH 3)	0.0181	0.9307
UV(pH 7)	0.0191	0.9382
UV(pH 9)	0.0251	0.9581
UV/ZnO(pH 3)	0.0251	0.9886
UV/ZnO (pH 7)	0.0281	0.9161
UV/ZnO (pH 9)	0.0381	0.9673

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